

BIOMATERIALS

UDC 620.22-419.8

APATITE-DIOPSIDE BIOGLASS CERAMIC COMPOSITES

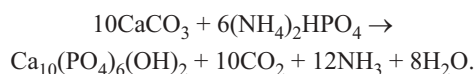
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The results of research into glass-ceramic materials for medical purposes are described. The effect of the liquid phase composition in the sintering of composites on the conversion of hydroxyapatite into tricalcium phosphate is determined. The possibility of controlling the structural-mechanical properties, bioactivity, and time of implant resorption by varying the ratio between hydroxyapatite and diopside glass ceramic in the composition of biological materials is demonstrated.

One of the targets of the contemporary science of materials is the development of materials for different functional purposes for medicine. In many cases a condition for successful application of ceramics and glass ceramics in dentistry and implant surgery is its biological activity, which is achieved by including hydroxyapatite $\text{Ca}_5(\text{PO}_4)_3\text{OH}$, which is a mineral analog of human bone, in the composition of bioceramics. This calcium-phosphate compound is a bioactive basis for most biomaterials.

Bioglass ceramics is promising for production of bone implants and defect fillers. The use of the bioactive component (hydroxyapatite) and crystallized glass in a composite makes it possible to combine sufficient porosity with high mechanical strength of material. The mechanical properties of artificial prosthesis should be adequate to actual loads on human bones or teeth [1]. The presence of porosity is essential for assimilation of bioceramics and its integration into bone tissue.

The synthesis of hydroxyapatite was conducted by the solid-phase-phase method according to the reaction



The study of the reaction products by the complex methods of thermal, x-ray phase, and IR-spectroscopic analysis demonstrated that hydroxyapatite with a ratio of Ca : P equal to 1.66(6) produced by firing at 1100°C with an exposure duration at the final temperature for 2 h and having the maximum phase homogeneity has the optimum properties for its further use in producing composite materials [2].

It is promising to use glass of diopside composition, which crystallizes under heat treatment in the course of sintering of a composite material, as a matrix for hydroxyapatite, since the diopside matrix is inert in relation to the organism, which at a certain stage is necessary for supporting soft tissues during biodegrading of the implant and regeneration of the bone. The bioactivity of the composite in this case will depend on its hydroxyapatite content.

The material used for production of diopside glasses was natural diopside mineral from the Slyudyanskoe deposit (Irkutsk Region) that has a high content of the principal mineral and a low quantity of impurities, which makes it suitable for biomedical purposes. The use of high-purity natural material lowers the production cost of implants.

In glass melting, natural diopside is preferable to pure oxides. The reactions of diopside formation in a batch based on pure oxides are rather difficult to implement. The amount of diopside formed at a temperature of 1300°C comprises 5 – 7%. In this case substantial quantities of SiO_2 , MgO , and CaO retain their original state up to the temperature of glass melting, which perceptibly hampers glass melting. The products of crystallization of glass based on pure oxides in addition to diopside include magnesium metasilicate and wollastonite. Due to the specific pyroxene structure of natural diopside, its structural groups persist in the melt and in glass in the production of glass ceramics, which ensures the high crystallization capacity of glass and its monomineral crystallization [1, 3].

The glass composition selected for research was the $\text{CaO} - \text{MgO} - \text{Al}_2\text{O}_3 - \text{SiO}_2$ system, which after complete crystallization was to form 75% crystalline phase, i.e., diopside, and 25% vitreous phase in the system $\text{CaO} - \text{Al}_2\text{O}_3 -$

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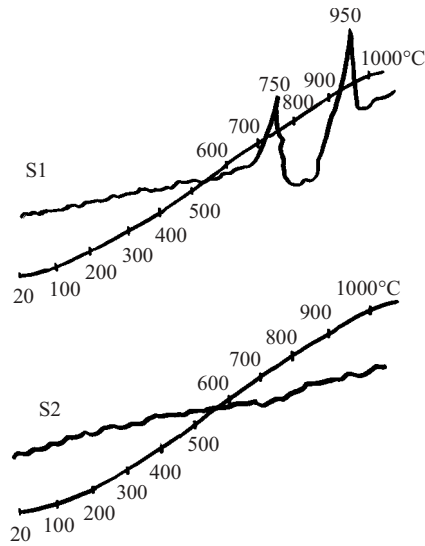


Fig. 1. Data of differential-thermal analysis of glasses of the diopside composition.

SiO_2 . The composition of experimental glasses S1 and S2 was as follows (here and elsewhere, wt.%): 60.45 SiO_2 , 22.17 CaO , 13.88 MgO , and 3.50 Al_2O_3 . In addition, 0.50% CaF_2 catalyst was introduced in glass S1.

This system was selected due to the necessity of introducing Al_2O_3 to decrease the crystallizing capacity of glass. The vitreous phase composition was selected based on the phase diagram for its melting point to be comparable to the melting point of the crystalline phase, i.e., diopside (1391°C). The vitreous phase composition was as follows (%): 75 SiO_2 , 11 CaO , and 14 Al_2O_3 .

In the production of glass ceramic materials the selection of a crystallization catalyst is significant, along with the glass composition. Catalysts that can be used in such systems are oxides of titanium(IV), zirconium(IV), molybdenum(VI), chromium(III), vanadium(V), and others. The use of calcium fluoride as the catalyst in the present study is due to subsequent application of this glass ceramic in medicine [4].

Glasses based on natural diopside were melted at a temperature of 1425°C for 1 h and poured into cold water to obtain granules.

The regularities of glass crystallization were studied by the differential-thermal analysis method (Fig. 1). The DTA curve of glass S1 has two clear peaks corresponding to exothermic effects at 750 and 950°C , the first effect being re-

lated to the formation of seeds that are crystallization centers and the second one to the process of crystal growth [5]. The DTA curve of glass S2 does not have perceptible peaks, which shows that this composition is unsuitable for production of glass ceramics.

According to DTA data of glass S1, a schedule for three-stage crystallization of bioglass ceramic composites was selected. The sintering temperature due to the formation of a residual vitreous phase was determined experimentally (Table 1). To study the regularities of crystallization, phase formation, and formation of properties in bioglass ceramics, compositions with a content of the bioactive hydroxyapatite component varying from 0 to 100% with an interval of 10% were selected. The compositions of the mixtures are listed in Table 2.

The shrinkage, porosity, and mechanical strength of bioglass ceramics depend on the composition and firing temperature. The porosity in the series of compositions $M_0 - M_{10}$ regularly increases with increasing content of hydroxyapatite (Fig. 2a). This is related to the fact that a decreasing content of initial glass in the mixture decreases the quantity of the residual vitreous phase in the composite, which is the active component in liquid-phase sintering and is responsible for an increasing amount of melt in its reaction with hydroxyapatite and earlier crystallized diopside. The quantity of hydroxyapatite passing into the melt depends both on the composite composition and on the firing temperature.

At 1150°C signs of overburning are found in samples of mixtures $M_1 - M_6$, which point to a narrow interval of the sintered state for these compositions. A consequence of overburning is a certain increase in porosity due to formation of microcracks and bursting of some bubbles. An increase in firing temperature to 1200°C leads to complete fusion of samples $M_1 - M_8$.

The highest bending strength (40 – 60 MPa) is observed in the composition corresponding to pure glass, which after crystallization represents a glass-ceramic matrix consisting of finely crystalline diopside bonded by the vitreous phase interlayers. As the content of hydroxyapatite in the mixture increases, the mechanical characteristics of sintered samples

TABLE 1

Stage	Temperature, $^\circ\text{C}$	Exposure duration, h	Processes in firing
I	750	1	Seed formation
II	950	2	Growth of crystals
III	1100	1	Sintering due to formation of residual vitreous phase

TABLE 2

Mixture	Weight content, %	
	hydroxyapatite	diopside glass
M_0	—	100
M_1	10	90
M_2	20	80
M_3	30	70
M_4	40	60
M_5	50	50
M_6	60	40
M_7	70	30
M_8	80	20
M_9	90	10
M_{10}	100	—

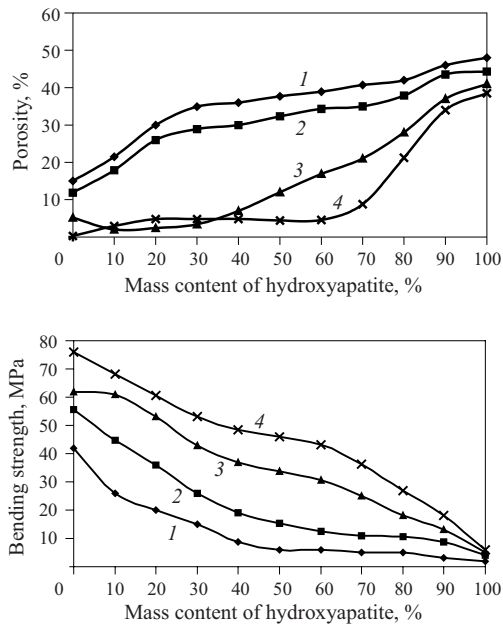


Fig. 2. Dependence of porosity and bending strength of bioglass ceramic samples on composition at sintering temperatures 1050 (1), 1100 (2), 1130 (3), and 1150°C (4).

decrease to 5–10 MPa. The variation in the compression and bending strength of samples is inverse to the variation in their porosity (Fig. 2b).

X-ray phase analysis indicates that crystallization of sample M_0 containing 100% glass at all firing temperatures does not produce any other phase apart from diopside. Samples of mixtures M_1 and M_2 after firing at 950 and 1000°C contain two crystalline phases, i.e., diopside and hydroxyapatite, and at temperatures above 1050°C only diopside.

In sample M_3 complete dissolution of hydroxyapatite and its conversion to the vitreous phase is observed at a temperature of 1100°C. Thus, the bioactivity of samples M_1 – M_3 containing diopside as their main crystalline phase is determined by the aluminocalcium-silicophosphate vitreous phase formed after assimilation of hydroxyapatite by the melt.

Samples M_4 – M_8 up to a firing temperature of 1130°C contain diopside and hydroxyapatite as the main crystalline phases, the relative intensity of reflections of these phases being proportional to the initial content of the components in the batch. At 1130°C hydroxyapatite partly transforms into tricalcium phosphate and at 1150°C only diopside and tricalcium phosphate are registered (Fig. 3). This is accounted for by the promoting effect of the liquid phase formed in firing on the rearrangement of the crystal lattice of hydroxyapatite and its transformation into tricalcium phosphate.

With a low glass content (mixture M_9) diopside reflections are absent on the x-ray phase diagram starting at a fir-

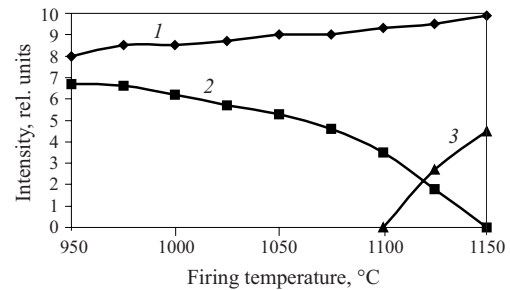


Fig. 3. Relative intensity of x-ray reflections in sample M_5 depending on firing temperature: 1) diopside; 2) hydroxyapatite; 3) tricalcium phosphate.

ing temperature of 1100°C. This is due to the modification of the melt composition after hydroxyapatite as well as diopside crystallized at the stage of devitrification pass into the melt. Secondary crystallization of diopside in cooling in the melt of such complex composition is hampered. Tricalcium phosphate identified starting at 1150°C reflects the part of hydroxyapatite that has recrystallized with participation of the liquid phase. The major amount of hydroxyapatite persists in the form of an unchanged crystalline component.

Mixture M_{10} retains hydroxyapatite as its main crystalline phase up to a sintering temperature of 1200°C. The absence of tricalcium phosphate in this composition corroborates the significant role of the liquid phase in crystallization and sintering of material.

Thus, a controlled ratio of hydroxyapatite and diopside glass in a composite material makes it possible to produce implants with different biological and physicomachanical characteristics (strength, porosity, bioactivity) required for specific medical purposes and with different times of material resorption, depending on the ratio between tricalcium phosphate and hydroxyapatite.

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